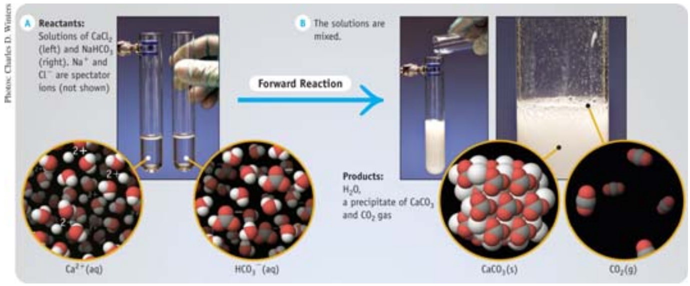
Principles of Chemical Equilibrium

15

Reaction Mixtures in Dynamic Chemical Equilibrium

- Reversible Reactions



A **Reactants:** Solutions of $CaCl_2$ (left) and $NaHCO_3$ (right). Na^+ and Cl^- are spectator ions (not shown)

B The solutions are mixed.

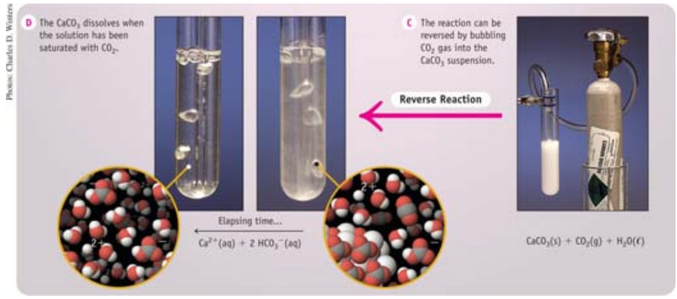
Products: H_2O, a precipitate of $CaCO_3$ and CO_2 gas

Photos: Charles D. Winters

$$Ca^{2+}(aq) + 2\ HCO_3^-\ (aq) \rightarrow CaCO_3(s) + CO_2(g) + H_2O(l)$$

Reaction Mixtures in Dynamic Chemical Equilibrium

- Reversible Reactions



D The $CaCO_3$ dissolves when the solution has been saturated with CO_2.

C The reaction can be reversed by bubbling CO_2 gas into the $CaCO_3$ suspension.

Photos: Charles D. Winters

$$Ca^{2+}(aq) + 2\ HCO_3^-\ (aq) \leftarrow CaCO_3(s) + CO_2(g) + H_2O(l)$$

Reaction Mixtures in Dynamic Chemical Equilibrium

- Reversible Reactions
  - Reversible chemical reactions can go in either direction, depending on the conditions.
  - Dynamic chemical equilibrium: a state in which the opposite reactions occur at equal rates so that there is no change of concentrations of species.

$$Ca^{2+}(aq) + 2\ HCO_3^-\ (aq) \rightleftharpoons CaCO_3(s) + CO_2(g) + H_2O(l)$$

- Net Reaction
  - The change of concentrations of species due to unequal rates of the reactions in opposite directions, when the system is not at equilibrium.

The Reaction Quotient and the Equilibrium Constant

- Reaction Quotient (Q)
  - For a reaction represented by $a\,A + b\,B \rightleftharpoons c\,C + d\,D$

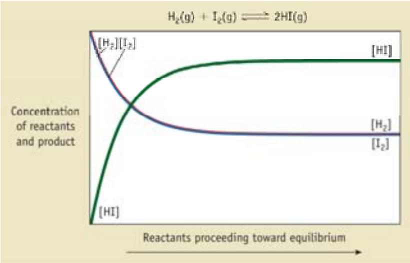
$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

EXAMPLE : Reaction between hydrogen and iodine gases at **425 °C** to produce hydrogen iodide gas

	H_2 (g)	+	I_2 (g)	⇌	2HI (g)	$Q = \frac{[HI]^2}{[H_2][I_2]}$
Initial (mol L^{-1})	0.0175		0.0175		0	0
Concentration at time 1 (mol L^{-1})	0.0150		0.0150		0.0050	0.111
Concentration at time 2 (mol L^{-1})	0.0100		0.0100		0.0150	2.25
Concentration at time 3 (mol L^{-1})	0.0037		0.0037		0.0276	56

The Reaction Quotient and the Equilibrium Constant

- Law of equilibrium: for a given reaction **at a specified temperature**, all equilibrium mixtures have the same value of the reaction quotient (*Q*). This numerical value of *Q* is called the **equilibrium constant** (*K*).



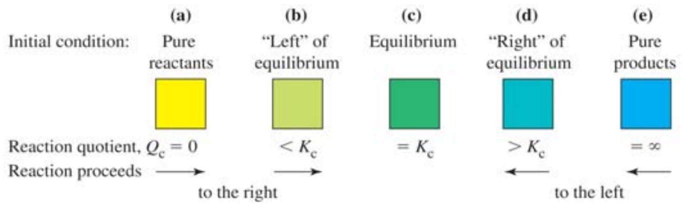
The Reaction Quotient and the Equilibrium Constant

- The form of *Q* and *K*
  - For reactions involving solids, concentration terms for the solids are not included in expressions for *Q or K.*
  - $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2\,(g)$ $Q = [CO_2]$
  - For reactions taking place in aqueous solution, the molar concentration of water is not included in expressions for *Q or K.*
  - $NH_3(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$ $Q = \frac{[NH_4^+][OH^-]}{[NH_3]}$

The Reaction Quotient and the Equilibrium Constant

- The Relationship between *Q* and *K* in Reaction Mixtures
  - Reactants and products: the species on the left and right sides of the written reaction equation, respectively.
  - ***Q* = *K*.** The reaction mixture is at equilibrium
  - ***Q* < K**. Equilibrium is attained if net reaction changes reactants into products.
  - ***Q* > *K***. Equilibrium is attained if net reaction changes products into reactants.

Reaction Quotient



Sample Exercise 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:

(a)
(b) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$
(c) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

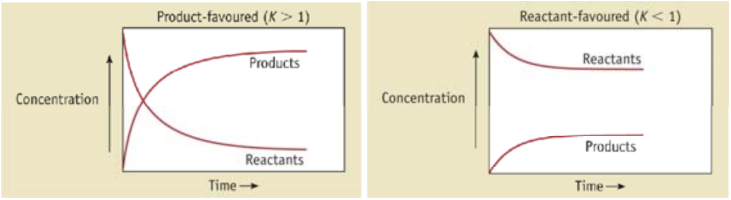
$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

Quotient and the Equilibrium Constant

- Spontaneous Reaction Direction, Stability, Gibbs Free Energy
  - Spontaneous direction of reaction: the direction in which net reaction occurs to bring a reaction mixture to equilibrium
    - ***Q* < K** reactants → products
    - ***Q* = K** reaction at equilibrium
    - ***Q* > K** products → reactants
  - As spontaneous reaction proceeds, the reaction mixture becomes more stable, reaching maximum stability at equilibrium.
  - Gibbs free energy is minimum at equilibrium.

Quantitative Aspects of Equilibrium Constants

- Magnitude of K and Extent of Reaction
  - Product-favoured reactions: *K* >> 1
  - Reactant-favoured reactions: *K* << 1
  -



Quantitative Aspects of Equilibrium Constants

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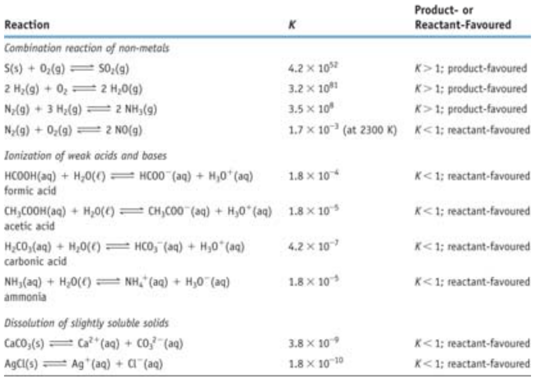

Reaction	K	Product- or Reactant-Favoured
Combination reaction of non-metals		
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	4.2×10^{52}	K > 1; product-favoured
$2\ H_2(g) + O_2 \rightleftharpoons 2\ H_2O(g)$	3.2×10^{81}	K > 1; product-favoured
$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$	3.5×10^{8}	K > 1; product-favoured
$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$	1.7×10^{-3} (at 2300 K)	K < 1; reactant-favoured
Ionization of weak acids and bases		
$HCOOH(aq) + H_2O(\ell) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$ formic acid	1.8×10^{-4}	K < 1; reactant-favoured
$CH_3COOH(aq) + H_2O(\ell) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$ acetic acid	1.8×10^{-5}	K < 1; reactant-favoured
$H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$ carbonic acid	4.2×10^{-7}	K < 1; reactant-favoured
$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + H_3O^-(aq)$ ammonia	1.8×10^{-5}	K < 1; reactant-favoured
Dissolution of slightly soluble solids		
$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	3.8×10^{-9}	K < 1; reactant-favoured
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}	K < 1; reactant-favoured

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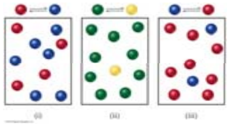
Sample Exercise Interpreting the Magnitude of an Equilibrium Constant

The following diagrams represent three systems at equilibrium, all in the same-size containers. **(a)** Without doing any calculations, rank the systems in order of increasing K_c. **(b)** If the volume of the containers is 1.0 L and each sphere represents 0.10 mol, calculate K_c for each system.



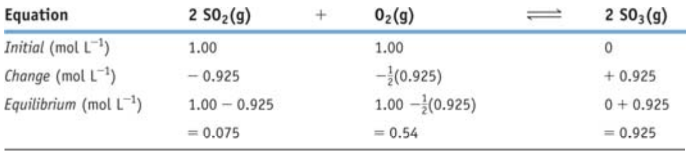
$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} \quad \begin{matrix} \longleftarrow \text{products} \\ \longleftarrow \text{reactants} \end{matrix} \qquad [15.8]$$

Sample Exercise Interpreting the Magnitude of an Equilibrium Constant

Continued

Aspects of Equilibrium Constants

- Estimating Equilibrium Constants
- If we know the concentrations of species in a reaction mixture at equilibrium, we can calculate the equilibrium constant at the temperature of measurement by substituting the concentrations into the reaction quotient.



Equation	$2\ SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\ SO_3(g)$
Initial (mol L^{-1})	1.00		1.00		0
Change (mol L^{-1})	− 0.925		$-\frac{1}{2}(0.925)$		+ 0.925
Equilibrium (mol L^{-1})	1.00 − 0.925 = 0.075		$1.00 - \frac{1}{2}(0.925)$ = 0.54		0 + 0.925 = 0.925

Equilibrium Constant *K* at 1000 K:

$$Q = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.925)^2}{(0.075)^2(0.54)} = 2.8\times10^2 = K$$

Quantitative Aspects of Equilibrium Constants

- Calculating Equilibrium Concentrations
- If we know the equilibrium constant of a reaction at the temperature of a reaction mixture and the starting concentrations of species, we can calculate the equilibrium concentrations of the species.

	$H_2(g)$	+ $I_2(g)$	$\rightleftharpoons$ 2 HI(g)
Initial concentration	(1 mol)/(0.500 L) = 2.00 mol L^{-1}	(1 mol)/(0.500 L) = 2.00 mol L^{-1}	0 mol L^{-1}
Concentration change	$-x$ mol L^{-1}	$-x$ mol L^{-1}	$+2x$ mol L^{-1}
Equilibrium concentration	$(2.00 - x)$ mol L^{-1}	$(2.00 - x)$ mol L^{-1}	$2x$ mol L^{-1}

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(2.00-x)(2.00-x)} = \frac{(2x)^2}{(2.00-x)^2} = K = 55.64$$

$$\therefore\ x = 1.58\ \mathrm{mol\,L^{-1}}$$

$$\therefore\ [H_2] = [I_2] = 2.00\ \mathrm{mol\,L^{-1}} - 1.58\ \mathrm{mol\,L^{-1}} = 0.42\ \mathrm{mol\,L^{-1}}$$

$$[HI] = 2 \times 1.58\ \mathrm{mol\,L^{-1}} = 3.16\ \mathrm{mol\,L^{-1}}$$

Reaction Equations and Equilibrium Constants

- Doubling the Reaction Equation
  - An equilibrium constant is specific for the chemical equation on which it is based.
  - If the coefficients of equation 1 are twice those of equation 2, K for equation 1 is the square of that for equation 2.

EXAMPLE *Equation 1*: $C(s) + ½\ O_2(g) \rightleftharpoons CO(g)$

Equation 2: $2\ C(s) + O_2(g) \rightleftharpoons 2\ CO(g)$

$$K_2 = \frac{[CO]^2}{[O_2]} = \left\{\frac{[CO]}{[O_2]^{1/2}}\right\}^2 = (K_1)^2$$

Reaction Equations and Equilibrium Constants

- Reversing the Reaction Equation
  - If the equation for an equilibrium reaction is the reverse of another, *K* for each reaction is the reciprocal of the other.

EXAMPLE

Equation 1: $HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^-(aq)$

Equation 2: $HCOO^-(aq) + H_3O^-(aq) \rightleftharpoons HCOOH(aq) + H_2O(l)$

$$K_1 = \frac{[HCOO^-][H_3O^+]}{[HCOOH]} \qquad K_2 = \frac{[HCOOH]}{[HCOO^-][H_3O^+]}$$

$$\therefore\ K_2 = \frac{1}{K_1}$$

Reaction Equations and Equilibrium Constants

- Deriving an Equilibrium Constant from Others
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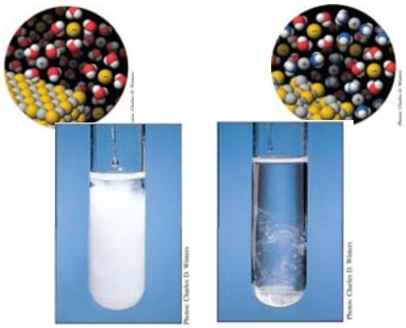


AgCl(s) in water

After adding $NH_3(aq)$

Dissolving solid silver chloride by adding ammonia.
(Left) A precipitate of AgCl(s) is suspended in water.
(Right) When a concentrated solution of ammonia is added, the ammonia reacts with the low level of $Ag^+(aq)$ ions in solution to form $[Ag(NH_3)_2]^+$ complex ions.

Equations and Equilibrium Constants

- Deriving an Equilibrium Constant from Others
- If we can add the equations of two or more reactions to obtain a balanced chemical equation for another reaction, *K* for the net reaction is the product of the equilibrium constants of the other reactions at the same temperature.

– **EXAMPLE**

– *AgCl (s) in water*: AgCl (s) ⇌ Ag^+ (aq) + Cl^- (aq) K_1

– *After adding NH_3(aq)* : Ag^+ (aq) + 2 NH_3 (aq) ⇌ $Ag(NH_3)_2^+$ (aq) K_2

– *Net*: AgCl (s) + 2 NH_3 (aq) ⇌ $Ag(NH_3)_2^+$ (aq) + Cl^- (aq) K_{net}

– $K_{net} = K_1 \times K_2$

Gases: The Equilibrium Constant, K_P

- Mixtures of gases are solutions just as liquids are.

$2\,SO_2(g) + O_2(g) \quad 2\,SO_3(g)$

Where P° = 1 bar

$$K_c = \frac{[SO_3]}{[SO_2]^2[O_2]} = \frac{\left(\frac{P_{SO_3}}{RT}\right)^2}{\left(\frac{P_{SO_2}}{RT}\right)^2 \frac{P_{O_2}}{RT}} = \frac{P_{SO_3}^{\ 2}}{P_{SO_2}^{\ 2}\ P_{O_2}}\ RT$$

$K_c = K_P(RT)$ $K_P = K_c(RT)^{-1}$

In general terms: $K_P = K_c(RT)^{\Delta n}$

Sample Exercise Evaluating an Equilibrium Constant When an Equation is Reversed

For the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

that is run at 25 °C, $K_c = 1 \times 10^{-30}$.Use this information to write the equilibrium-constant expression and calculate the equilibrium constant for the reaction

$$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

Sample Exercise Combining Equilibrium Expressions

Given the reactions

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad K_c = 6.8 \times 10^{-4}$$

$$H_2C_2O_4(aq) \rightleftharpoons 2\,H^+(aq) + C_2O_4^{2-}(aq) \qquad K_c = 3.8 \times 10^{-6}$$

determine the value of K_c for the reaction

$$2\,HF(aq) + C_2O_4^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)$$

Sample Exercise Combining Equilibrium Expressions

Continued

Pure Liquids and Solids

- Equilibrium constant expressions do not contain concentration terms for solid or liquid phases of a single component (that is, pure solids or liquids).

$$C(s) + H_2O(g) \quad C \rightleftharpoons H_2(g)$$

$$K_c = \frac{[CO][H_2]}{[H_2O]^2} = \frac{P_{CO}P_{H_2}}{{P_{H_2O}}^2} \quad (RT)^1$$

Disturbing Reaction Mixtures at Equilibrium

- The condition of chemical equilibrium may be “disturbed” such that $Q \neq K$
  - Changing concentrations at a given temperature, which results in a change in Q
  - Changing temperature, which results in a change in K

- **Le Chatelier’s principle**
- If the condition of equilibrium of a reaction mixture is disturbed by either a change of concentrations of species, or by change of temperature, then the relative concentrations of reactants and products will change in such a way as to minimize the imposed change.

Disturbing Reaction Mixtures at Equilibrium

- Effect of Changing Concentrations
  - Adding or removing reactants or products

EXAMPLE: Add butane to a reaction mixture with butane and isobutane in equilibrium at 25 °C. The equilibrium constant at 25 °C is 2.5.

	Butane	**⇌ Isobutane**
Initial (mol L^{-1})	**0.500**	**1.25**
Concentration immediately on adding butane (mol L^{-1})	**0.500+1.50 =2.00**	**1.25**
Change in concentration to re-establish equilibrium (mol L^{-1})	***-x***	***+x***
Equilibrium (mol L^{-1})	**2.00 - *x***	**1.25 + *x***

$$Q = \frac{[\text{isobutane}]}{[\text{butane}]} = \frac{1.25 + x}{2.00 - x} = K = 2.5$$

$\therefore \; x = 1.07 \text{ mol L}^{-1}$

$\therefore$ After equilibrium is re-established

$[\text{butane}] = 2.00 - x = 0.93 \text{ mol L}^{-1}$

$[\text{isobutane}] = 1.25 + x = 2.32 \text{ mol L}^{-1}$

Disturbing Reaction Mixtures at Equilibrium

- Effect of Changing Concentrations
  - Adding or removing reactants or products

If reagents are added to, or removed from, an equilibrium mixture so that $Q < K$, then equilibrium would be re-established by net reaction of reactants to products (increasing Q).

This is consistent with application of Le Chatelier's principle.

Disturbing Reaction Mixtures at Equilibrium

- Effect of Changing Concentrations
  - Changing the Volume of a Gas-Phase Reaction Mix
    - A volume decrease (*increase*) of a gaseous reaction mixture at equilibrium will lead to a new equilibrium condition by net reaction that results in a decrease (*increase*) in the number of molecules in the system.
    - For a reaction in which there is no change in the number of molecules when reaction occurs, a volume change will not lead to a change in the relative amounts of reactants and products, because the equality $Q = K$ will not be disturbed.

Apply Le Chatelier's principle

Consider the change of concentration caused by the volume change

Not the volume change itself!

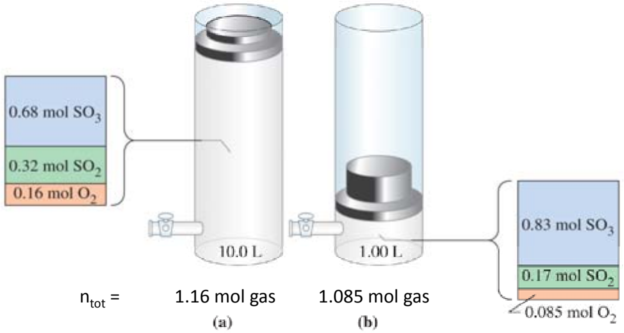
Effect of Change in Volume

$$K_c = \frac{[G]^g[H]^h}{[C]^c[D]^d} = \frac{n_G^g \quad n_H^h}{n_A^a \quad n_B^a} V^{(a+b)-(g+h)}$$

$$= \frac{n_G^g \quad n_H^h}{n_A^a \quad n_B^a} V^{-\Delta n}$$

- When the volume of an equilibrium mixture of gases is *reduced*, a net change occurs in the direction that produces *fewer moles of gas*. When the volume is *increased*, a net change occurs in the direction that produces *more moles of gas*.

Effect of the Change of Volume



	(a)	(b)
n_{tot} =	1.16 mol gas	1.085 mol gas
K_p =	415	338

Effect of Condition Changes

- Adding a gaseous reactant or product changes P_{gas}.
- Adding an inert gas changes the total pressure.
  - Relative partial pressures are unchanged.
- Changing the volume of the system causes a change in the equilibrium position.

$$K_c = \frac{[SO_3]}{[SO_2]^2[O_2]} = \frac{\left(\frac{n_{SO_3}}{V}\right)^2}{\left(\frac{n_{SO_2}}{V}\right)^2 \frac{n_{O_2}}{V}} = \frac{n_{SO_3}{}^2}{n_{SO_2}{}^2 \; n_{O_2}} \; V$$

Disturbing Reaction Mixtures at Equilibrium

- Effect of Changing the Temperature
  - Endothermic reactions
    - K increases as temperature is raised
    - Immediately after the temperature of a system at equilibrium is raised, Q < K
    - A new equilibrium condition would be attained by net reaction of reactants to products.
  - The opposite is the case for exothermic reactions

Consistent with Le Chatelier's principle

Disturbing Reaction Mixtures at Equilibrium

- Effect of Changing the Temperature

The tubes in the photograph both contain gaseous NO_2 (brown) and N_2O_4 (colourless) at equilibrium.

- K is larger near 0 °C (right), so the system contains relatively high concentration of the colourless $N_2O_4(g)$.
- At 50 °C (left), K is smaller, and the reaction mixture contains a relatively high concentration of NO_2 , as indicated by the darker brown colour.

Effect of Temperature on Equilibrium

- *Raising the temperature* of an equilibrium mixture shifts the equilibrium condition in the *direction of the endothermic* reaction.
- *Lowering the temperature* causes a shift in the *direction of the exothermic* reaction.

Effect of a Catalyst on E

- A catalyst changes the mechanism of a reaction to one with a lower activation energy.
- A catalyst has no effect on the condition of equilibrium.
  - But does affect the *rate* at which equilibrium is attained.

Sample Exercise Using Le Châtelier's Principle to Predict Shifts in Equilibrium

Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta H^\circ = 58.0\ \text{kJ}$$

In which direction will the equilibrium shift when **(a)** N2O_4 is added, **(b)** NO_2 is removed, **(c)** the pressure is increased by addition of $N_2(g)$, **(d)** the volume is increased, **(e)** the temperature is decreased?

Sample Exercise Predicting the Effect of Temperature on *K*

(a) Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

(b) Determine how the equilibrium constant for this reaction should change with temperature.

Sample Exercise Calculating *K* When All Equilibrium Concentrations Are Known

After a mixture of hydrogen and nitrogen gases in a reaction vessel is allowed to attain equilibrium at 472 °C, it is found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant K_p for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Sample Exercise Calculating *K* from Initial and Equilibrium Concentrations

A closed system initially containing 1.000×10^{-3} *M* H_2 and 2.000×10^{-3} *M* I_2 at 448 °C is allowed to reach equilibrium, and at equilibrium the HI concentration is 1.87×10^{-3} *M*. Calculate K_c at 448 °C for the reaction taking place, which is $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

Sample Exercise Calculating *K* from Initial and Equilibrium Concentrations

Continued

Sample Exercise Predicting the Direction of Approach to Equilibrium

At 448 °C the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

is 50.5. Predict in which direction the reaction proceeds to reach equilibrium if we start with 2.0×10^{-2} mol of HI,
1.0×10^{-2} mol of H_2, and 3.0×10^{-2} of I_2 in a 2.00-L container.

Sample Exercise Calculating Equilibrium Concentrations

For the Haber process, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $K_p = 1.45 \times 10^{-5}$ at 500 °C. In an equilibrium mixture of the three gases at 500 °C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

Sample Exercise Calculating Equilibrium Concentration from Initial Concentrations

A 1.000-L flask is filled with 1.000 mol of $H_2(g)$ and 2.000 mol of $I_2(g)$ at 447 °C. The value of theequilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

at 448 °C is 50.5.What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?

Sample Exercise Calculating Equilibrium Concentration from Initial Concentrations

Continued